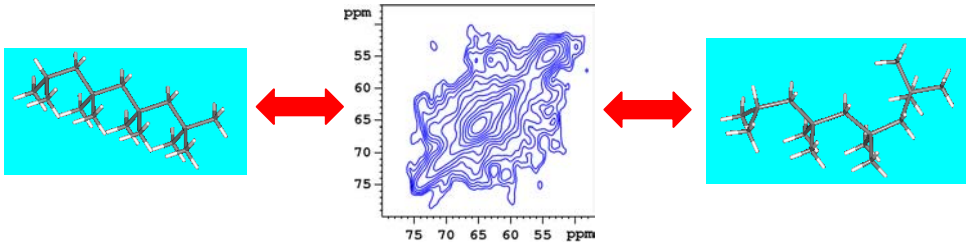
Experimental Impetus for New Mixing Rules in Polymers: Lessons from Polyolefins

Jeffery L. White, North Carolina State University, DMR-0137968

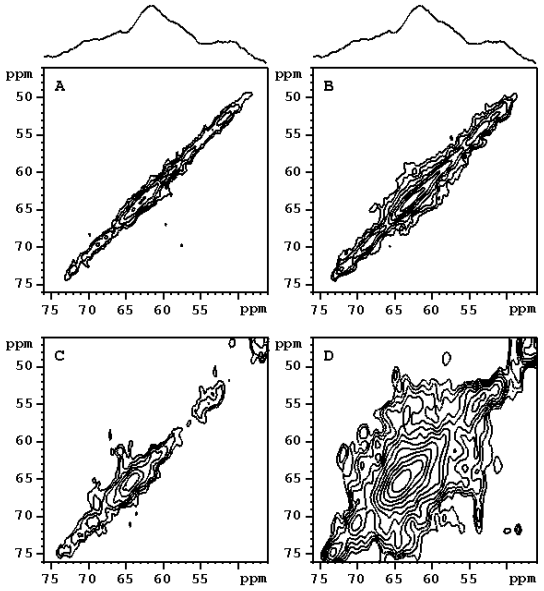
Society benefits from the development of new, inexpensive polymer blends for use in food packaging, medical containers, building materials, and automobiles. We have provided new experimental insight into the solid-state phase behavior of polyolefin blends, which heretofore have been poorly understood. Solid-state NMR experiments show that configurational entropy is a key driving force for miscibility in certain polyolefin blends, which suggests a new theoretical framework for predicting miscibility in these polymers.

Macromolecules **36**, 4844 (2003).

J. Am. Chem. Soc. **in press** (2003).



Basic experimental strategy (above), in which 2D solid-state NMR, obtained at the glass transition temperature, shows conformational interchange taking place. Here, 4 seconds is required at the calorimetric Tg of polyisobutylene to obtain the equilibrium exchange pattern, indicating complete conformational rearrangement.



Two-dimensional MAS ^{13}C exchange spectra (left) of the PIB methylene region (50-80 ppm) at 208 K for (a) neat PIB with 100 millisecond mixing time, (b) neat PIB with 1 second mixing time, (c) PIB/PEB-23 blend with 1.5 second mixing time, and (d) PIB/PEB-66 blend at 100-ms mixing time. The key point is that the time for conformational rearrangement is greater than an order of magnitude shorter in the miscible blend (d), relative to the pure PIB (a) or the immiscible blend (s). Quantitative treatment via Adams-Gibbs theory indicates that the total increase in configurational entropy exceeds 3.

Experimental Impetus for New Mixing Rules in Polymers: Lessons from Polyolefins

Jeffery L. White, North Carolina State University, DMR-0137968

Education:

Two Ph.D. graduate students (Justyna Wolak and Xin Jia) and one postdoctoral fellow (Xingwu Wang) contributed to this work. Undergraduate Matthew Truitt, a former Dreyfus Undergradate Fellow and now a Ph.D. student in the PI's group, also worked on this project. Graduate student Wolak has presented her results at one national ACS meeting (New Orleans), and two local ACS meetings. Xin Jia has presented his contributions at the international Experimental NMR Conference.

Outreach:

On approximately 15 different occasions, the PI has presented demonstrations to local elementary and middle school, as well as Boy Scout and church groups, on the physical properties of molecules. Of particular relevance to this project is the discussion, and demonstration, of the "like dissolves like" rule, which is violated for macromolecules like polyolefins. Students take great pleasure in knowing that even scientists sometimes can't understand what at first appears to be a simple problem.